

ENVIRONMENTAL PROTECTION

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TITANATE COMPOSITES FOR CORE CATCHER DONOR MATERIAL IN A NUCLEAR REACTOR

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Composites based on titanates compositions have been selected and tested. A technology for their production is proposed using high-alumina cement. Estimate of some of their properties is supplied making it possible to use these composites as donor materials in a reactor core catcher.

In case of a serious failure in a nuclear reactor, there is a risk of core melting and melted corium leaking into the ambient medium. To protect environment from the radioactive effect in the case of an emergency, the reactors currently designed or constructed are provided with core catchers [1]

To diminish the effect of aggressive melt on a core catcher, donor materials (DM) are placed in it that contain Fe_2O_3 , SiO_2 , Al_2O_3 , titanate concrete, etc. [2–4].

A donor material is needed to weaken a thermomechanical impact on protective coating, to condition the melt, and in melt cooling to form a matrix resembling geological materials in the core catcher, which would retain the majority of radionuclides and be resistant to the ambient medium effect (RF Patent No. 2187852). It is recommended to use several crystalline phases simultaneously as DM, which can be obtained in reactions between the core materials, the donor and refractory layers.

A comparison of crystalline, glass, and cement matrices revealed the advantages of crystalline matrix regarding their chemical resistance and durability [5]. The most promising can be a mineral-resembling matrix. An example of such matrix is a group of materials of the synroc type developed on the basis of multiphase titanate ceramics of the following composition [6]: (here and elsewhere in wt.%): 69.5–71.4 TiO_2 , 6.5–9.8 ZrO_2 , 5.5–9.6 Al_2O_3 , 5.6–8.5 BaO , and 11.0–14.5 CaO .

The main phases of synroc are perovskite $\text{CaO} \cdot \text{TiO}_2$ and zirconolite $\text{CaO} \cdot \text{ZrO}_2 \cdot 2\text{TiO}_2$. Zirconolite has high re-

sistance to atmospheric effects, exceptional radiation resistance, and a capability of forming solid solutions within a wide interval of concentrations. There are data [7] that natural zirconolite may contain substantial quantities of uranium and thorium dioxide and oxides of rare-earth elements. All this indicates that crystalline matrices containing zirconolite are promising as DMs. Synroc demonstrated good results for disposal of radioactive waste.

There are various methods for producing synrocs described in the literature [6], which require high energy consumption and expensive machinery.

We investigated the processes of production and properties of DM based on a multiphase titanate matrix implemented according to the concrete technology, which makes it possible to produce single elements (bricks, plates, profiled products) and to develop solid lining of different sizes.

The initial materials were titanium dioxide TiO_2 of grade R-02 ($\geq 93\% \text{TiO}_2$), zirconium dioxide ZrO_2 that is waste of fianite production ($\geq 99\% \text{ZrO}_2$ of cubic modification), barium carbonate BaCO_3 and calcium carbonate CaCO_3 of the analytical grade, barium sulfate BaSO_4 , aluminum oxide Al_2O_3 , barium titanate BaTiO_3 of grade “pure”, barium-aluminum cement (BAC) (at least $95\% \text{BaAl}_2\text{O}_4$), high-alumina cement HAC-75 and HAC-70 (at least $98\% \text{calcium aluminates}$).

The DM compositions considered are listed in Table 1 (oxides) and Table 2 (initial components). Compositions were selected based on a prescribed synroc composition by varying contents of TiO_2 and ZrO_2 in a wide range. Calcium, barium, and aluminum oxides were introduced mainly via cements BAC and HAC with a respective recalculation.

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TABLE 1

DM composition	Mass content, %				
	TiO ₂	ZrO ₂ stabilized Y ₂ O ₃	BaO	CaO	Al ₂ O ₃
Synroc B*	66.1	1.5	9.2	17.1	6.1
I	71.4	6.5	5.6	11.0	5.5
II	39.8	23.7	10.5	6.5	19.5
III	24.0	54.0	6.3	3.9	11.8

* Synroc B also contained 8.1% cement HAC-70.

TABLE 2

DM composition*	Mass content, %				
	TiO ₂	ZrO ₂ cubic modification	CaCO ₃	Al ₂ O ₃	HAC-75
Synroc B	63.1	6.0	18.0	5.1	—
I	64.1	5.9	16.5	—	7.1
II	39.0	23.7	4.0	—	16.4
III	23.2	52.4	—	0.1	15.0

* Besides, Synroc B contained 7.8% BaTiO₃, composition I — 6.4% BaCO₃, composition II — 17.2% BAC, composition III — 9.3% BaSO₄.

Mixtures for samples were prepared by dry mixing of initial materials. Samples were produced by semidry molding or ramming into molds. In molding the binder was a 5% aqueous PVA solution and in ramming the binder was water, whose quantity was calculated based on the quantity of the binder and the water-to-cement ratio of a normal paste thickness for the particular cement, which was 10–12% (above 100%). Curing was implemented first in an enclosed volume in a moist atmosphere up to 3–7 days, then in air under a moist tissue.

Samples I and III were prepared with preliminary firing of all initial finely dispersed components except for cement (BAC and HAC-75) to obtain the granular component. For this purpose, a mixture was prepared by dry mixing, then briquettes were compressed at specific pressure of 30–50 MPa and fired in air at a temperature of 1570–1650 K with a 2-h exposure. After firing, the briquettes were crushed, the powder was screened into fractions of 2.5–0.63 and below 0.63 mm. For making experimental samples, coarse-grained powders were mixed with cement in certain proportions,

mixed with water and rammed into molds. After 3–5 days of curing in moist-air conditions, the samples were taken out of molds and left to cure for a required time in enclosed volumes.

The compression strength was determined on cube-shaped samples of size 30 × 30 × 30 mm, apparent density and open porosity were determined by the kerosene-saturation method or calculated based on cylindrical samples 20 mm in diameter and 15–20 mm high. The same samples were used in melting on a Uran plant [6]. X-ray phase and petrography analysis were carried out on powder samples using the standard methods.

Composition I (Table 2) that is close to synroc B was used to make a DM without firing and with preliminary firing of initial finely disperse components, for the purpose of obtaining a granular filler. Some properties and the phase composition of DM depending on the heat treatment temperature were estimated (part of DM samples of composition I after curing were heat-treated in air at 1500 and 1900 K with exposures of 40 min and 13 h at the end temperature, respectively). It can be seen from Table 3 that DM after curing has sufficient strength and does not have shrinkage. Heating to 1500 C significantly increases strength, density, and shrinkage, which is presumably related to batch sintering. A perceptible weight loss is registered, which leads to formation of open porosity. Treatment at a temperature of 1900 K with a long exposure (approximately 13 h) causes an abrupt increase in porosity of DM samples (up to 50%) with weight loss over 90%. DM samples on substrate of zirconium dioxide ceramics acquired an irregular rounded shape and were traversed by pores. Indentations of rounded samples 0.5 to 1.5 mm deep impregnated with melt were registered in the substrate.

X-ray phase analysis indicates substantial differences in the phase composition of DM after heat treatment at 1530 and 1920 K. Heating to 1530 K ensures only a start of the formation of synroc phases: zirconolite, hollandite, and ZrO₂ of the cubic modification. An increase in the heat treatment temperature to 1920 K and a lengthy exposure results in the fact that TiO₂ is present in the sample as the main phase, and the phases of hollandite, and titanates of aluminum, barium, and zirconium are present in small quantities. The presence of high porosity in DM samples and indentations in the substrate under the samples corroborate the formation of a fluid melt at high temperatures and its flowing out of samples into the ZrO₂ substrate. The DM in this case is depleted of

TABLE 3

DM	Compression strength, MPa	Apparent density, g/cm ³	Open porosity, %	Weight loss, %	Linear shrinkage, %	Phase composition (x-ray phase analysis)
After 7 days of curing	2.5–3.5	1.9–2.2	—	—	0	Not determined
After heat treatment*	21–22	3.22	18–20	13–14	15–20	TiO ₂ , ZrO ₂ of cubic modification, BaTi ₄ Al ₂ O ₁₂ , CaZrTi ₂ O ₇ , etc.

* At 1530 K for 40 min.

low-melting compounds. The results of the experiments demonstrates the possibility of the formation of main synroc phases of the selected composition already at a temperature of 1533 K. An increase in the treatment temperature above the melting point and its protracted effect may cause the DM melt penetrating into the bottom refractory layers and partial evaporation of some compounds.

Composition I was used to test a technology with preliminary sintering of all components except for cement HAC. The intent was to further use the granular sintered component to produce a DM according to the concrete technology (with cement). After the briquettes were fired at 1600 K with a 2-h exposure in an oxidizing atmosphere, x-ray phase analysis identified the presence of the following phases: main phases: barium titanates of different compositions and cubic modification of ZrO_2 , small quantities: TiO_2 , $CaZrTi_2O_7$, and others.

The following composition of DM (%) was taken for experiments: 50.0 sintered DM with particle size 0.63 – 2.5 mm, 42.9 sintered DM with particle size below 0.63 mm, 7.1 cement HAC-75, about 12.0 water (above 100%).

Properties of DM samples after curing for 7 – 10 days

Compressive strength, MPa	0.8 – 1.6
Apparent density, g/cm^3	2.5 – 2.7
Open porosity, %	22 – 24
Thermal resistance, number of thermal cycles without destruction:	
1470 K – air	> 10
1470 K – water	1

An increase in cement content up to 10% raises the compressive strength of DM up to 15 MPa after 7 days of curing.

Next, compositions II and III with a higher content of ZrO_2 filler were tested. The introduction of aluminum and barium oxides and a majority of calcium oxide was carried out taking into account their contents in cements BAC and HAC. An addition of a greater amount of binder (over 30%) did not significantly modify the technology of producing DM from finely dispersed powders.

Material of composition II after curing for more than 2 months had compression strength 11 – 12 MPa, apparent density approximately $2.36 g/cm^3$, and open porosity about 25%.

Composition III was used to determine a rational amount of mixing water and the effect of curing duration on properties of DM produced from finely dispersed powders. A rational amount was determined as 11.5 – 12.0% water (above 100%), which allows for making DM with high compressive strength (about 25 MPa) and open porosity approximately 14% after 14 days of curing (Table 4). An optimum curing duration, when DM acquires optimum properties, is 30 days in air-moist hardening. The compressive strength in this case is about 28 MPa and density grows up to $3.19 g/cm^3$. These parameters are reached due to cement-curing processes (for-

TABLE 4

Parameter	DM composition III	
	without sinter	with sinter
Compressive strength, MPa, after 13 – 16 days of curing depending on the quantity of admixed water W (above 100 %):		
7.0%	2.3	13.0 ($\tau_{cur} = 7$ days)
10.0%	17.7	–
11.5%	24.7	–
17.0%	10.8	–
25.0%	2.6	–
Compressive strength, MPa, with $W = 11.5\%$ and curing duration τ_{cur} :		
7 days	13.0	13.0 ($W = 6 - 7\%$)
14 days	24.7	–
30 days	27.8	–
90 days	25.0	–
150 days	–	16.0
Apparent density g/cm^3 , with $W = 11.5\%$ and curing duration τ_{cur} :		
14 days	3.12	3.08* ($\tau_{cur} = 7$ days)
30 days	3.19	–
Open porosity, %, with $W = 11.5\%$ and curing duration $\tau_{cur} = 14$ days	14.4	–
TCLE in temperature interval of 273 – 1073 K $^{-1}$	–	9.4×10^{-6}
Heat capacity, * J/(kg · K)	551	–
Thermal conductivity, * W/(m · K)	3.75	–
Heat resistance (for thermal cycles 1773 K – air), number of thermal cycles:		
at $W = 11.5\%$	1	–
at $W = 25.0\%$	Destruction in the form of explosion	–

* Data were obtained in calculation.

mation of a sufficient quantity of HAC crystal hydrates, which together with the filler form a dense and strong stone).

Composition III was used to prepare sinter consisting of TiO_2 , Al_2O_3 , and $BaSO_4$. The firing temperature was 1650 K. X-ray phase analysis identified the presence of barium aluminates of different compositions and free TiO_2 . The sinter and the other components (ZrO_2 , HAC) were used to prepare a DM of the following composition (%): 52.4 electromelted ZrO_2 with particle size below 2.5 mm, 32.6 sinter ($TiO_2 + Al_2O_3 + BaSO_4$) with particle size below 2.5 mm, 15.0 cement HAC-75, and 6.0 – 7.0 water (above 100%).

It can be seen from the data in Table 4 that DM samples after 6–7 days of curing have parameters close to these of the material prepared without preliminary sintering.

The thermophysical properties listed in Table 4 (heat capacity and thermal conductivity) were calculated according to the method described in [9], and other properties were measured according to the standard method.

Samples were prepared from initial components (compositions synroc B and I) according to the method described.

Melting was carried out in oxidizing conditions on a Uran light-heating plant [8] ensuring temperatures above 2300 K. A test sample was placed on a ZrO_2 substrate, which was put on a water-cooled copper plate. The temperature rise proceeded in 5 min to 1650 K, then at a rate of 100 K/min rose to the beginning of melting of the sample, next, went up in 6 min to 1920 K, after which the plant was switched off.

After melting, the samples were studied by x-ray and petrography analysis. X-ray phase analysis revealed that a multiphase system is formed in cooling, which contains a cubic modification of ZrO_2 as the main phase, zirconolite $\text{CaZrTi}_2\text{O}_7$, perovskite CaTiO_3 , and hollandite $\text{BaTi}_2\text{Al}_2\text{O}_{12}$ as complementary phases, and barium titanate, aluminum titanate, and rutile TiO_2 in small quantities. According to petrographic analysis, crystallization of the melt occurs rather fast, and an amorphous phase coexists with crystals in the form of intercrystalline interlayers up to 2 μm thick. The main matrix consists of homogeneous isometric crystals sized up to 12 μm . Inside this matrix, phases of crystals sized from 2 to 4 μm crystallize in the form of rounded agglomerations from 8 to 30 μm . The amorphous phase is present in the form of discontinuous interlayers up to 2 μm thick. There are elongated pores around the matrix crystals.

The melting temperature of samples of the type of synroc B is 1670 ± 30 K.

Melting of DM samples of composition synroc B with a 30-min exposure indicated that the material differs from samples melted without exposure. It is well crystallized, there is virtually no amorphous phase (its minimal quantity is 2–3 vol.%), the crystals of the cubic and other phases have a larger size: up to 60 μm . The ratio of these phases is 50 : 50. A phase with the perovskite structure is present, which crystallizes in the forms of large prismatic crystals. Eutectics are registered, which contain crystals of monoclinic and rhombic syngony of size up to 4 μm . According to the x-ray phase analysis data, an exposure facilitates a decrease in the number of the crystalline phases. The main phases are hollandite, zirconolite, and perovskite, whereas TiO_2 , ZrO_2 and Al_2TiO_5 phases are present in small quantities. All initial barium titanate was fixed in a phase of the hollandite type.

In melting on a Uran plant, a temperature gradient was observed across the sample height. The phase composition varied across the height as well. The chemical analysis of synroc B samples determined that the highest-melting phases, i.e. zirconolite and rutile predominantly crystallize

on the surface. Phases containing Al and Ba are virtually not identified on the surface, they penetrate into the substrate. The content of perovskite varies across the sample height and grows, as the melt penetrates into depth, since the content of CaO in the bottom part of the sample is nearly twice as much as in its upper part; the quantity of TiO_2 is high as well.

Testing of composition I of DM was implemented on samples of various types: a mixture of finely disperse components without thermal treatment; with heat treatment at 1533 K, and with a granular filler previously sintered.

The testing schedule was as follows: temperature rise at a rate of 350 K/min up to the formation of a melt drop, fusion over the whole upper surface of the sample, exposure at 2070–2170 K for 20–30 min, and natural cooling with the plant switched off.

No significant difference in the behavior of various types of samples on the Uran plant was registered.

The following phenomena were observed: a start of melting, i.e., formation of single melt drops at 1873–1930 K, intense melting with the formation of a melt mirror within a temperature interval of 1970–2020 K, further melting up to 1/4–1/2 of the sample height with melt boiling and evaporating at temperatures from 2070 to 2170–2220 K. When the plant was switched off, an uncontrolled temperature decrease occurred and crystallization of melt was often accompanied by cracking of the sample. The x-ray phase analysis of a sample preheated to 2170–2220 K and melted from its surface indicated that the main phases were TiO_2 (rutile) and $\text{BaTi}_4\text{Al}_2\text{O}_{12}$ (a hollandite-type phase). The secondary phases were $\text{CaZrTi}_2\text{O}_7$, $\text{Ba}_2\text{Ti}_9\text{O}_{20}$, and ZrO_2 of the cubic modification.

Thus, after melting DM of the synroc composition, some of its phases crystallize in cooling, however, zirconolite and perovskite have not been registered as the main phases.

The method of measuring phase transformation temperatures is based on a fast registration of temperature in free cooling of the tank with melt, whose thickness is a few tenths of millimeter, formed on the surface of a flat ceramic sample placed vertically and heated for 6–16 sec by concentrated radiation of CO_2 -laser in the ambient air atmosphere [10]. The upper limit of temperature, from which cooling started, was determined by a possible effect of the products of melt evaporation condensing and spilling from the sample on the measurement results. The maximum temperature did not exceed 2350 K.

The temperature of the sample was registered using a single-range two-channel photodiode pyrometer with logarithmic amplifiers. The pyrometer was graduated based on radiation of a black body model comparing it with a ÉOP-66 standard visual optical pyrometer.

Altogether four experiments were conducted for synroc, which differed in the duration of sample heating and accordingly, in the melt thickness. The maximum heating temperature in different experiments varied from 2175 to 2350 K.

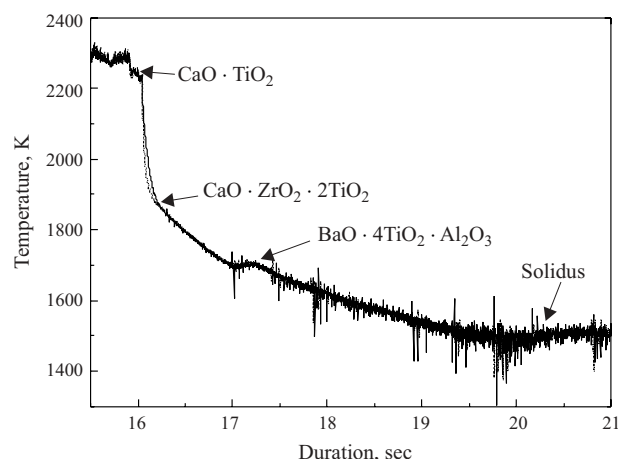


Fig. 1. Cooling thermogram of a sample of synroc B.

During the heating and especially after reaching a quasi-stationary temperature state, significant non-monotonic temperature changes were registered, which is probably related to a redistribution of individual components in the melt. The minimum temperature registered was 1480–1500 K. The heating duration of various samples was 6, 10, and 16 sec.

The cooling curves of four samples of synroc B from a temperature under 2300 to 1500 K have a virtually identical course. Figure 1 shows several characteristic segments, which can be correlated with the crystallization temperatures of the main mineral-like phases of synroc. At a temperature above 2300°C a melt exists, from which perovskite $\text{CaO} \cdot \text{TiO}_2$ may crystallize at 2230–2250 K, which is evidenced by the presence of a “shelf” on the curve at this temperature. Next, the temperature decreases dramatically to about 1850 K and then more smoothly from 1850 to 1700 K. In this temperature interval another phase of the zirconolite type $\text{CaO} \cdot \text{ZrO}_2 \cdot 2\text{TiO}_2$ can crystallize from the melt. The temperature “shelf” at 1690–1700 K can be identified as a eutectic and as transformation to the crystalline state of the phase resembling hollandite $\text{BaO} \cdot 4\text{TiO}_2 \cdot \text{Al}_2\text{O}_3$. A protracted temperature plateau in the range of 1500 K is clearly observed in cooling in all experiments. In this range a final transition from liquid to solid phase takes place, i.e., crystal-

lization of the whole melt. The average value (based on four experiments) of the solidus temperature of for the melt of this composition was 1490 K.

As a consequence of studies performed, titanate compositions have been proposed, specifics of their production technology have been investigated, and some properties have been estimated, making it possible to use them as donor materials for a core catcher in a nuclear reactor.

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